hydrous sodium sulfate, poured back into the distilling flask and the crude epichlorohydrin thus freed from water fractionated again. After a small forerun the pure epichlorohydrin distilled at 30–32° under 10 mm. pressure; the yield was 770 g. of epichlorohydrin or 80% of the theoretical. The epichlorohydrin thus obtained boiled at 115–117° and had a specific gravity of 1.18 at 20°.

(b) **Epibromohydrin.**—One liter (2140 g.) of dibromohydrin was suspended in 1.5 liters of water and then gradually under shaking 420 g. of calcium hydroxide was added in the course of fifteen minutes. Then 420 g. of calcium hydroxide was added at once and the epibromohydrin distilled under reduced pressure in the same manner as is described in the case of epichlorohydrin. The united lower layers of two distillations (690 + 70 = 760 cc.) were fractionated under 50 mm. pressure and the medium fraction, after drying with anhydrous sodium sulfate, fractionated again. The yield of epibromohydrin (b. p. 61–62° under 50 mm. pressure or 134–136° at ordinary pressure) was 1200 g. or 90% of the theoretical. The product had a specific gravity of 1.665.

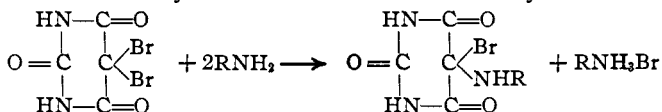CONTRIBUTION FROM
THE FLEISCHMANN LABORATORIES
NEW YORK, N. Y.
RECEIVED OCTOBER 15, 1931
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GÉZA BRAUN

COMMUNICATIONS TO THE EDITOR

THE REACTION OF DIBROMOBARBITURIC ACID WITH AMINES

Sir:

In a recent communication Nightingale and Schaefer[1] describe the reaction of 5,5-dibromobarbituric acid with primary and secondary amines. The reaction is said to yield a series of 5-bromo-7-alkyl uramils.

$$\begin{array}{ccc} \text{HN---C=O} & & \text{HN---C=O} \\ \text{O=C} \quad \text{C}\underset{\text{Br}}{\overset{\text{Br}}{<}} + 2RNH_2 \longrightarrow & \text{O=C} \quad \text{C}\underset{\text{NHR}}{\overset{\text{Br}}{<}} + RNH_3Br \\ \text{HN---C=O} & & \text{HN---C=O} \end{array}$$

Such a reaction seems improbable in view of the general properties of the class of "persubstituted" halogen compounds.[2] Such compounds act as brominating agents, the active halogen being replaced by hydrogen. To quote a single example, bromonitromalonic ester reacts with dimethylamine to form the amine salt of nitromalonic ester and N-bromodimethylamine.[3] Baeyer[4] and Biltz and Hamburger[5] obtained the ammonium

[1] Nightingale and Schaefer, THIS JOURNAL, **54**, 236 (1932).

[2] *Cf.* a summary by Schmidt, Ascherl and von Knilling, *Ber.*, **59**, 1876 (1926), which includes over seventy references to the literature.
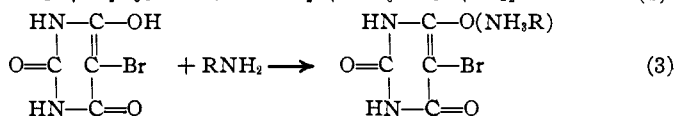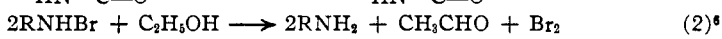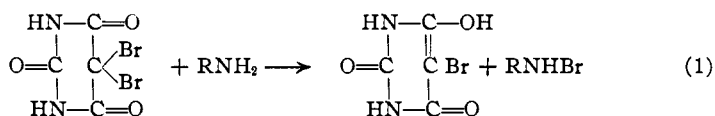
[3] Willstätter and Hottenroth, *Ber.*, **37**, 1776 (1904).

[4] A. Baeyer, *Ann.*, **130**, 134 (1864).

[5] Biltz and Hamburger, *Ber.*, **49**, 641 (1916).

salt of monobromobarbituric acid on treating dibromobarbituric acid with aqueous ammonia.

From a consideration of the above evidence it seemed probable that the compounds reported by Nightingale and Schaefer were not 5-bromo-7-alkyl uramils, but merely the amine salts of 5-bromobarbituric acid. The authors mention the fact that their products are decomposed by alkalies with the liberation of the amine. This would be a very unusual reaction for a substituted uramil, since uramil itself is hydrolyzed slowly by alkalies into urea and aminomalonic acid. The liberation of the amine would be expected, however, on treating alkyl ammonium 5-bromobarbiturates with alkali. These salts lack but two hydrogen atoms of being isomeric with the uramils; consequently the nitrogen and bromine analyses which constitute the only proof of structure offered by Nightingale and Schaefer could be explained by either formula. From results reported[3] in the literature it would seem that the formation of these salts could be accounted for by the reactions

$$
\underset{\substack{|\\HN-C=O}}{\overset{\substack{HN-C=O\\|}}{O=C}}\ \underset{}{C}\!\!\begin{array}{c}{}^{Br}\\{}_{Br}\end{array}\ +\ RNH_2 \longrightarrow\ \underset{\substack{|\\HN-C=O}}{\overset{\substack{HN-C-OH\\|\ \ \|}}{O=C}}\ C\,Br\ +\ RNHBr \qquad (1)
$$

$$
2RNHBr\ +\ C_2H_5OH\ \longrightarrow\ 2RNH_2\ +\ CH_3CHO\ +\ Br_2 \qquad (2)^6
$$

$$
\underset{\substack{|\\HN-C=O}}{\overset{\substack{HN-C-OH\\|\ \ \|}}{O=C}}\ C-Br\ +\ RNH_2 \longrightarrow\ \underset{\substack{|\\HN-C=O}}{\overset{\substack{HN-C-O(NH_3R)\\|\ \ \|}}{O=C}}\ C-Br \qquad (3)
$$

In order to establish the structure of the compounds prepared by Nightingale and Schaefer their work was repeated with ethylamine, di-n-propylamine and di-n-amylamine. The products agreed in physical properties with those which they reported, and all of them were decomposed immediately by cold 10% sodium hydroxide with the liberation of the amine. Such a rapid reaction is characteristic of the liberation of an amine from a salt, and not of the splitting of a nitrogen to carbon linkage. The reaction was carried out quantitatively in one case. The di-n-propylamine salt (1 g.) was treated with an excess of cold 20% sodium hydroxide and the free amine extracted with ether. The amine was extracted from the ether solution with dilute hydrochloric acid, the extract being placed in a Kjeldahl apparatus and made alkaline with 20% sodium hydroxide. The amine was determined by distillation into an excess of standard acid: required, 32.47 cc. of 0.1 N sulfuric acid, or 100.03% calcd. The titrated solution was evaporated to dryness and dipropylamine dipropyldithiocarbamate prepared as a derivative; m. p. 118–118.5°, mixed with a known

⁶ Reaction 2 is not essential to the formation of the salts, but merely indicates the method by which the amine is regenerated; *cf.* Biltz and Behrens, *Ber.*, **43**, 1984 (1910); Berg, *Ann. chim.*, (7) **3**, 339 (1894).

specimen gave no depression. Monobromobarbituric acid was obtained from each of the salts by a procedure similar to that employed by Biltz and Hamburger[5] with the ammonium salt. Yields of 30–50% of pure 5-bromobarbituric acid were obtained; m. p. 215–216°;[7] Br calcd., 38.61; found, 38.90. The loss is due to the solubility of the sodium salt and the instability of 5-bromobarbituric acid in aqueous solution.[7]

The products obtained by Nightingale and Schaefer have thus been demonstrated to be alkyl ammonium 5-bromobarbiturates. The "dark tarry oils" which they obtained with dibromobarbituric acid and aromatic amines were formed in a similar bromination process; such experiments have been reported previously in the literature. Dibromobarbituric acid and aniline give monobromobarbituric acid and p-bromoaniline,[8] while with dimethylaniline monobromobarbituric acid and p-bromodimethylaniline are obtained.[9]

[7] Bock, *Ber.*, **55**, 3401 (1922).
[8] Conrad and Reinbach, *ibid.*, **35**, 522 (1902).
[9] Gupta and Thorpe, *J. Chem. Soc.*, **121**, 1898 (1922).

DEPARTMENT OF CHEMISTRY   ARTHUR C. COPE
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RECEIVED JANUARY 20, 1932
PUBLISHED MARCH 5, 1932

CESIUM FILMS ON TUNGSTEN

Sir:

When cesium atoms strike a tungsten filament at high temperature (filament surrounded by negatively charged cylinder), every atom is ionized. At lower temperature the number of adsorbed atoms (adatoms) per unit area (σ) can be measured by flashing the filament and allowing the evaporated atoms to strike a second parallel filament from which they evaporate as ions. The potentials of the two filaments are so chosen that no ions escape from the first but all escape from the second. A galvanometer ballistic kick gives a quantitative determination of σ.

Dr. J. Bradshaw Taylor has developed this method for measuring the rates of evaporation of atoms (ν_a), ions (ν_p) and electrons (ν_e) as functions of σ and T. The following conclusions are drawn.

The tungsten surface, after considerable heating at 2800°K., is homogeneous, except that a small fraction (0.0050) can hold adatoms more firmly than the rest. With rising pressure, and a filament at 1100–1200°K., the first atoms are adsorbed on this active surface, which becomes saturated before 0.5% of the remaining surface is occupied. The active spots are separate spaces holding one atom each from which the heat of evaporation is 80 Kg. cal. per g. atom. The following refers to the homogeneous surface.

With low filament temperatures and high pressures, σ reaches a limit σ_1 $= 3.563 \times 10^{14}$ atoms per sq. cm. of true surface (34% greater than apparent surface) corresponding to a monatomic film with one Cs atom for four tungsten atoms. The electron emission at constant T reaches a maximum at $\Theta = \sigma/\sigma_1 = 0.67$.

From the data on ν_a, by Gibbs' adsorption equation, the spreading force F (dynes. cm.$^{-1}$) can be calculated and the two-dimensional equation of state is $F = \sigma_1 kT\Theta/(1 - \Theta) + F'$. Using the virial of the force f acting at a distance r between adatoms: $F' = 0.25 \, \sigma\Sigma(rf)$. The forces are strong repulsove forces varying as r^{-4}. The adatoms constitute dipoles, whose moment M decreases as Θ increases by the depolarizing force of neighboring adatoms. It is deduced theoretically (without adjustable parameters) that

$$F' = 3.338 \, M^2\sigma^{5/2} + 1.531 \times 10^{-5} \, M^{4/3}T^{1/3}I\sigma^2$$

I being an integral which decreases from 0.893 to 0 as Θ increases from 0 to 1. From experimental values of F it is found that $M = 16.3 \times 10^{-18}$ at $\Theta = 0$, this coefficient decreasing to 9.8 at $\Theta = 0.3$ and 7.6 at $\Theta = 0.6$. The contact potential $V = 2\pi\sigma M$ can thus be calculated from ν_a, agreeing with direct measurements and with values calculated from

$$\ln \nu_e = 63.44 - (11606/T)(4.760 - V)$$

V being in volts.

The experimental values of ν_a give

$$\ln[\nu_a(1 - \Theta)/\Theta] - 1/(1 - \Theta) = A - B/T$$

where

$$A = 61 + 4.8 \, \Theta - 2.4 \, \Theta^2$$

and

$$B = 32380/(1 + 0.714 \, \Theta)$$

The thermodynamic relation

$$\ln(2\nu_p) = \ln \nu_a + (11606/T)(V_w - V_i - V)$$

gives ν_p (in agreement with experiment), where $V_i = 3.874$ volts (ionizing potential of Cs) and $V_w = 4.622$ (work function for W).

From these equations ν_a, ν_e, ν_p and V are calculable, as functions of T and Θ (up to 0.65), from a curve giving $M(\Theta)$ and from V_i, V_w and the heat of evaporation of adatoms from a bare tungsten surface, 63.5 Kg. cal. per g. atom (2.757 volts).

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IRVING LANGMUIR

THE HYDROGEN NUCLEUS OF MASS 2 (ISOHYDROGEN NUCLEUS p_2e) AS A UNIT IN ATOM BUILDING

Sir:

On the basis of the fact that the formula[1] $(p_2e)_z$ represents the most abundant atomic nuclei, and because the formula p_2e represents the general increment in composition of nuclei of odd atomic weight, the writer has considered the nuclear group p_2e to play a fundamental role in atom building. Also such a particle was supposed to possess a great advantage over the alpha particle as a unit in atom building since, on account of its smaller charge, it much more readily penetrates the potential wall around a complex nucleus. A part of this point of view is presented in fragmentary quotations from papers published[2] in 1921 and 1923. "Electron groups in which one negative electron alone is present may be even more fundamental in a certain sense" than the p_2e_4 group or alpha particle, "especially since the group p_2e corresponds to the minimum value of N/P for a nucleus stable both with respect to disintegration by ordinary means, and moderately stable with regard to aggregation" (*i. e.*, union with other nuclei). "If p_2e is the fundamental group, as the general considerations suggest, then its low abundance may be explained as due to the pairing of the negative electrons, two p_2e groups changing into one alpha particle." "The first step in the formation of an alpha particle may be the union of two protons with one electron to form the group p_2e, which is very difficult to break up, but readily unites with a like group to form an alpha particle. Sometimes it may add to a complex nucleus." The newer data give additional support to this idea. All atomic species may be divided into four series (Table I).

TABLE I

1. Even ($2R$) Series	2. Odd ($2R + 1$) Series
$(p_2e)_R es$	$(p_2e)_R (pe) es$
A. Thorium ($4\,M$)	R = either odd or even
R = even, S = even	if S = odd or even
B. Uranium	A. Beryllium ($4\,M + 1$)
R = odd, S = odd	B. Actinium (?) ($4\,M + 3$)
R, S, M = whole numbers	

The matching or non-matching of R and S in evenness or oddness is of fundamental importance.

TABLE II

DIFFERENCE OF COMPOSITION ON ANY LEVEL OF CONSTANT ISOTOPIC NUMBER (S = CONSTANT)

Level	Even series	Odd series
Zero	p_2e	p_2e
1 to 26	p_4e_2 $(= \alpha)$	p_2e

[1] p = a proton, e = an electron, z = atomic number, P = atomic weight or number of nuclear protons, N = number of nuclear electrons.

[2] *Phil. Mag.*, **42**, 334 (1921); THIS JOURNAL, **45**, 1426–1433 (1923).

The even series are merely extensions of the radioactive series, *since any level represents a series of alpha changes* (Fig. 1 and Table II).

All levels of the odd, and the zero level of the even, series exhibit the difference p_2e.

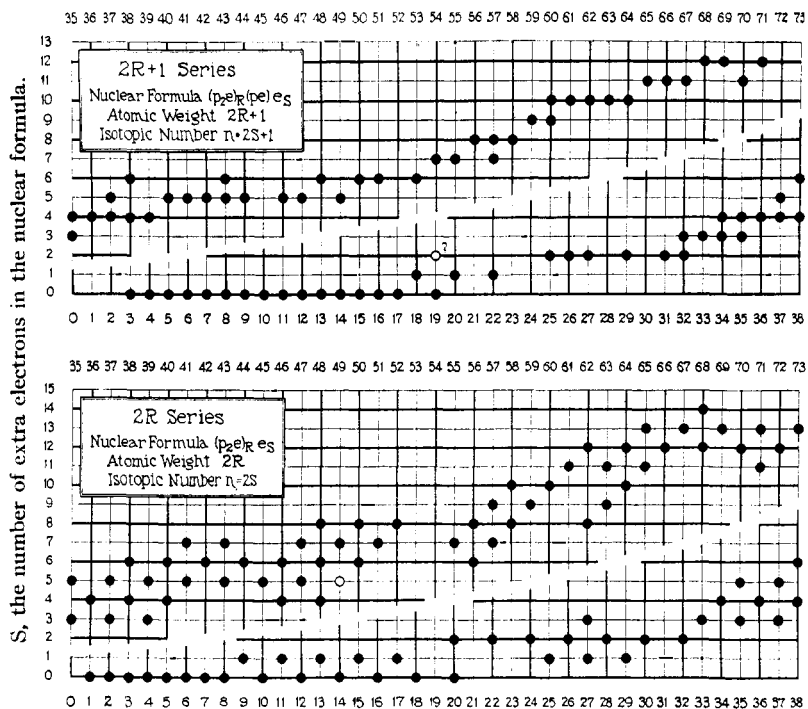It is remarkable that every possible multiple of p_2e from 1 to 8 is now known.[3]

Fig. 1.—R, the number of p_2e units in the nuclear formula (atomic number $Z = R - S$).

The isohydrogen nucleus may be formed by the collision of a proton with a permanent or temporary neutron (pe), or by a three body single collision. In the latter case the wave length emitted should be about 0.001 Å. The nuclear spin of p_2e is probably zero, but may be unity in units $h/2\pi$, while that of the neutron should be $1/2$. There is much evidence which indicates that in the nucleus groups of the composition p_2e do not, in general, remain independent, but that they merge by doubling into units of the composition of alpha particles.

[3] Recent discoveries are: beryllium isotope $(p_2e)_3$, Watson and Parker, *Phys. Rev.*, **37**, 167 (1931); and a higher isotope of hydrogen, F. Allison (American Chemical Society meeting, September, 1931), and about 1/4000 of hydrogen of mass 2 in hydrogen, Urey, Brickwedde and Murphy, *Phys. Rev.*, **39**, 154 (1932).

The extra electrons of the formulas (Fig. 1) are therefore not the "extra" or "loose" electrons of the nuclues. The correct values of these are given in another paper (*Phys. Rev.*, **38**, 1280–1282 (1931).

It may be supposed that in the building up of complex atomic nuclei the following particles may attach themselves to an atomic nucleus provided they penetrate its potential wall: protons, electrons, neutrons if they exist, p_2e particles and alpha particles.

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RECEIVED FEBRUARY 2, 1932
PUBLISHED MARCH 5, 1932

CRYSTALLIZATION VELOCITIES

Sir:

Although it has long been known that the rate of crystallization from supercooled melts is greatly dependent on the particular compound used, the effect of molecular symmetry has not been investigated up to the present time. If there is such an effect, it should be most easily discoverable with organic compounds, whose structures may be postulated from x-ray and dipole moment measurements.

Recent measurements here on the linear crystallization velocity indicate that the symmetry of the molecule largely determines the rate of transition from liquid to solid. The maximum linear velocities of the most illustrative examples so far measured are tabulated.

MAXIMUM LINEAR VELOCITIES

Compound	Rate in mm. per minute	Melting point, °C.	Supercooling, °C.
o-Dichlorobenzene	2,200	−17.6	25
m-Dichlorobenzene	700	−24.8	25
p-Dichlorobenzene	20,000	52.9	25
1,2,4-Trichlorobenzene	25	17	25
1,3,5-Trichlorobenzene	7,500	63.4	26
1,1,2-Triphenylethane	Less than 1	54.0	50
1,1,1-Triphenylethane	77	94.8	33
1,2-Diphenylethane	700	51.2	34
1,1-Diphenylethylene	16	8.2	25
Diphenylmethane	530	25.1	27
Triphenylmethane	27	93.6	29

In view of the recent revival of interest in the subject of crystallization, this preliminary report is being given at this time to avoid possible wasteful duplication. It is planned to discuss the complete results in a paper later.

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